CONCERNING

INJURIOUS CONSTITUENTS IN WHISKY

AND THEIR RELATION TO FLAVOUR

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CONCERNING INJURIOUS CONSTITUENTS IN WHISKY AND THEIR RELATION TO FLAVOUR.

SOME 18 months ago in these columns [1] we drew attention to the physiological action of furfural, a universal constituent of both raw and matured pot-still whisky, and also to the apparently different physiological effects of whisky containing and freed from aldehydes. Since then the successful application on the large scale of a method, indicated in our last communication, for removing the aldehydes from whisky during distillation has brought this subject prominently before pharmacologists and chemists. We therefore think that it will be not without interest to enter somewhat more fully into the probable effects of removing the aldehydes and the higher alcohols from whisky than was possible in our last article. More especially is this the case since it must now be regarded as established that *at least some* of the raw and offensive smell and taste of freshly distilled whisky are due to its aldehydes. The knowledge of this fact is directly due to our original investigations, and although these were initiated from a purely pharmacological standpoint, this by-result—viz., the effect upon the flavour of raw whisky of the removal of the aldehydes—is likely to be of practical importance.

As is well known, the whisky that is generally sold to-day is blended whisky—that is, a mixture of spirits of various kinds. Blending consists essentially of mixing whisky derived entirely from malt and made in a pot-still, often of very varying age, with so-called silent spirit, or spirit obtained by the fermentation of various materials and the distillation of the subsequent wort, this latter usually being accomplished in a Coffey-still—i.e., in a still provided with a rectifying column. Silent spirit is cheaper than pure malt whisky not only on account of the materials from which the

[1] THE LANCET, Dec. 8th, 1900, p. 1643.

former is produced but also because it requires less maturing.[2] Whisky, on the other hand, derived from malt and made in a pot-still is when raw a very nauseating and foul-smelling liquid. Upon being kept in wood for varying periods of time it becomes changed in character, the irritating smell and disagreeable taste disappearing and the spirit assuming, according to its original properties, a more or less marked bouquet. By suitably blending these two varieties of whisky the trade are able to produce a drinkable article at a relatively cheap price. The alcohol percentage is rendered more or less constant by dilution with water and the colour of the liquid is brought up to a uniform artificial tint by means of caramel or some other suitable agent.

From this very superficial sketch it will be evident that whisky can only very rarely be strictly termed pure, consisting, as it does, of a drink the basis of which is generally pure whisky, this latter being artificially doctored to suit the public taste and the distiller's pocket. It is essential to bear this in mind because an improvement by chemical means of the manufacture of whisky is apt on account of its title to create prejudice; this should not be so since subsequently to fermentation the whole manufacture of whisky, whether in pot-still or in Coffey-still, is essentially a chemical process, and if the chemistry of it cannot at the present time be followed step by step it is due in no small degree to the fact that the employés in distilleries are neither chemists themselves nor are they in the majority of cases even directed by chemists. When chemical knowledge has eventually permeated into the distilleries in the Highlands then we shall certainly know more of the minute chemistry of whisky than we do now.

In its essentially chemical character whisky differs at once from wine: a wine can go on "living" long after it is laid in the winebin, can live and change even up to the time it is poured into its penultimate resting-place—the wineglass of the consumer. In the ageing of wine we have biological and chemical processes to consider, in the maturing of whisky chemical and chemico-physical ones. Wine-producers have never hesitated to utilise all that physics, chemistry, and biology can do for them; champagne is frozen and wines are pasteurised and, if need be, sugared or plastered; the manufacture of whisky stands still, and distillers exorcising any improved method with the epithet "doctor" view with mistrust any technique other than the one adopted by their forefathers.

[2] The amount of maturation required by silent spirit before it is fit for blending varies. The rectifying column is theoretically supposed to keep back from the distillate all substances boiling above 79° C. As the whole operation is conducted under considerable pressure this theoretical result is not always accurately attained. The usual rectifying apparatus seems to be more efficient in removing higher alcohols, &c., than in getting rid of some of the lower boiling-point impurities; thus acetic aldehyde can generally be detected in patent-still spirit but furfural with its boiling point of 162° is most rarely if ever present.

There are, however, other reasons more cogent than the above why any process for the improved manufacture of whisky should be welcomed by pharmacologists and, indeed, hygienists. It has been pointed out on many occasions that whisky is by no means free from injurious constituents other than alcohol. It is also true that whisky is not simply alcohol but differs very considerably from it, at least in taste. Whether it differs also pharmacologically is not so clear. There is no doubt that wines influence digestion according to their acidity, bouquet, &c., but this has not been shown with regard to whisky.[3] That the effect of whisky upon the system is simply that of its ethyl alcoholic content is perhaps not strictly true, though there is very considerable physiological evidence in favour of this thesis. Be this as it may, we all prefer, at least all whisky-drinkers, whisky to correspondingly diluted ethylic alcohol. The difference between the two is essentially one of so called by-products. It is also to the class of by-products that the injurious constituents of whisky belong. It is true that these substances are present in very small quantities. Our information, however, upon this point is largely derived from German sources. In Germany pot-stills are practically non-existent, and it is to whisky produced in these stills that our remarks especially refer.

That whisky does contain injurious substances other than ethylic alcohol is shown by the sudden death of an employé in a West of England distillery. This unfortunate man died suddenly after imbibing a quantity of "feints." A post-mortem examination revealed the fact that his stomach contents had a similar odour to amyl nitrite. Although there was no evidence of the chronic effects of alcohol upon the liver, &c., there was evidence of acute irritant poisoning. The medical man who reported the case inferred that death was probably due to amylic alcohol.[4] A sensation of throbbing and headache was recently experienced by one of the authors

[3] Chittenden and his collaborators have made many experiments upon this subject. Their earlier experiments were made upon digestions *in vitro* and showed that, in so far as whisky was concerned, the only instance in which it differed materially from ethylic alcohol was in its influence upon pancreatic digestion. Here it exerted a marked inhibitive action, much greater than that produced by ethylic alcohol of the same strength. According to these observers, however, subsequent experiments made *in vivo* showed that the above experiments *in vitro* had not much practical value. *In vivo* whisky behaved practically identically with ethylic alcohol of the same strength.—Vide Chittenden and others: American Journal of Medical Sciences, 1896, January-April, pp. 35, 163, 314, 431; also American Journal of Physiology, 1898, vol. i., p. 164.

[4] Swain: Brit. Med. Jour., 1891, vol. i., p. 903. It must be, however, noted with regard to this death that the "feints" consumed undoubtedly contained aldehydes, and that the poisonous nature of the aldehydes was apparently unknown to the author. The inclusion in this paper of an explanation of technical terms would render it too long; the reader is referred on this subject to, *inter alia*, the following:—Allen, Commercial Organic Analysis, vol. i.; Matthews, Alcoholic Fermentation; and Moercke, Handbuch der Spiritus Fabrication.

of this paper and others upon inhaling the vapour arising from the low-wines and feints in a pure malt whisky distillery.

If, then, certain of the by-products of whisky are injurious to the consumer the question naturally arises, Are these individual by-products necessary? If this question be answered in the negative the conclusion which must be drawn is that whisky would be much better without them. This matter is of further interest in that at least one of the assumed effects of maturation is to diminish the amount of these substances present. From this it follows that any improved method for the manufacture of whisky which prevents the formation of these substances or at least keeps them out of the finished product performs one of the functions of maturation. At the present time there is, however, some difference of opinion as to to what class of chemical substances the injurious constituents of whisky belong and as to the precise relation between them and those substances which give to whisky its characteristic and agreeable flavour. Many observers have shown that iso-amylic alcohol, the main constituent of the so-called fusel oil, is much more poisonous than ordinary ethylic alcohol. Analytical results, although discrepant,[5] point to the conclusion that the quantity of fusel oil in matured spirit is considerably less than that in the raw substance. Coincidently with this diminution in fusel oil during maturation the flavour of the whisky improves. The taste of fusel oil itself when suitably diluted is not, however, unpleasant and this substance is actually used for the purpose of giving a whisky taste to silent spirit. The amount of fusel oil calculated as amylic alcohol present in whisky, whether raw or matured, is practically always under 0·1 per cent., and it thus follows that although these higher alcohols are much more poisonous than ethylic alcohol, yet nevertheless in the quantities present they would under ordinary circumstances hardly affect to an appreciable degree the action of the spirit.[6] However, if they are not necessary whisky is better without them.

Acting upon the above assumption many attempts have been made to remove fusel oil from raw whisky. It is to be noted that these attempts have all been directed specifically to the fusel oil itself, although it is more than probable that certain other constituents to be considered below though not aimed at have been affected by these processes. The *rationale* of certainly the earlier of these processes has been to obtain rapidly that oxidation which is supposed, upon not very certain grounds, to take place gradually during so-called "natural" maturation. This artificial oxidation has been brought about by very varying methods, all of

[5] Allen: Evidence before Select Committee, 1891. Also Bell: Evidence before same Committee.

[6] In some analyses at present unpublished and made while this paper was passing through the press, the percentage of higher alcohols reached 0·25 per cent.

which, however, have not only promoted—as, indeed, does natural maturation—oxidation *per se* but also evaporation. It must be noted here that in the evaporation of a complicated liquid like whisky those substances will have the greatest tendency to escape which have the lowest boiling-point. The higher alcohols do not possess this property. Nevertheless, however high the boiling point of a given constituent of whisky may be some of it will escape. Under these circumstances it is difficult in judging of these artificial maturation processes, as indeed of so-called natural maturation, to know how much of the effect to ascribe to evaporation and how much to oxidation.[7] Recently, however, a process for the artificial maturation of whisky, primarily intended for the removal of fusel oil, has been patented which certainly owes its result entirely to forced evaporation. This process is certainly as successful, if not more so, than those combining evaporation with oxidation. We have had especial facilities of examining the product of this last-named process and there is no doubt that by means of it raw whisky is deprived in the course of half an hour or so of its raw and offensive smell. Analyses of the treated spirits show that the greatest change which they have undergone is a diminution in their fusel oil content.

If, however, we come to examine this so-called defuselised whisky we find that it approaches more or less closely to silent spirit, that is, pure ethylic alcohol, in character. In other words, the spirit has by the process lost some of the essential attributes of whisky. This fact leads us to a consideration of the relation between the higher alcohols and the bouquet-giving constituents of whisky. That there is a relation between these two sets of bodies is practically universally admitted since there is strong evidence that the alcoholic constituents of fusel oil, amylic, propylic, and butylic alcohols are largely concerned in the production of the compound ethers which have actually been isolated from whisky or old whisky casks. Valeric ether is one of the few bouquet-giving substances which has actually been obtained from grog.[8] Another substance having the aroma of jargonelle pears is butyric acetate. This is produced from butyric alcohol and acetic acid, the latter being formed by the oxidation of ethylic alcohol, either in the fermenting back or subsequently.[9]

[7] These considerations are especially of interest with regard to furfural or the compound ethers. Furfural boils at 162°, ethyl acetate at 73° (lower than ethylic alcohol), and amyl acetate at 137° (*vide infra*).

[8] Lindet: Comptes Rendus, cxii., 102. Allen: Organic Commercial Analysis, vol. i., p. 149.

[9] Another consideration which should not be neglected in this connexion is that these higher alcohols are biological as distinguished from chemical products. They are produced in the fermentation backs at the end of fermentation and probably depend for their origin chiefly upon those conditions of yeast life occurring as a consequence of the disappearance of the sugar. Further, the species of ferment used seems to affect the character of the higher alcohols produced.

It must not be assumed, however, that the substances above named are the only ones to which the flavour of good old whisky is due. Rich malt whisky when perfectly raw contains free acids of the fatty series and also compound ethers. There is further analytical evidence to show that the actual development of compound ethers in the cask during maturation is slight;[10] in other words, that it is the compound ethers which were originally present that bestow upon the matured whisky its eventual flavour. If we accept this view we must assume that the maturation of whisky consists not so much in a process characterised by the development through oxidation of bouquet-giving substances as in the disappearance or change in the nature of bodies which mask the flavour of the compound ethers originally present. One fact seems quite certain—viz., that a whisky originally poor in fatty acids and compound ethers never develops into a full-bodied whisky.

Another class of compounds present in whisky both raw and matured and which have up to the present attracted but little attention are the aldehydes. The most recent process invented for the improvement of whisky manufacture consists in the extraction, by chemical means, of the aldehydes from the low wines. This is done by transforming them into hydrazones. These substances being non-volatile do not pass over upon the subsequent distillation of the low wines; by this means the raw whisky is rendered entirely free from aldehydic bodies. The interesting point of this process is that by means of it only the aldehydes and the acetals (compounds of the aldehydes with alcohols) are removed; the higher alcohols, fatty acids and compound ethers are left intact. Raw whisky treated in this way loses practically entirely its pungent and irritating taste and smell. This fact must lead us to reconsider the view which has been up to the present universally adopted—viz., that the characteristic smell and taste of raw whisky are due to the higher alcohols. This obviously cannot be so, as the new whisky produced in the above manner—i.e., from dealdehyded low wines—although containing the higher alcohols has no pungent taste or flavour. We must, therefore, now ascribe the pungency of raw whisky either to aldehydes or to acetals.

Concerning the actual aldehydes present in whisky either raw or matured very little is known; until quite recently no accurate method of estimating them has been available. Concerning their amount it may be said that as much as 20 milligrammes of aldehydes have been found in 100 cubic centimetres of German Branntwein.[11] One aldehyde, however, furfural, has for a long time attracted the attention of chemists and pharmacologists. The reason for this most probably is that this substance gives a very delicate colour

[10] Bell: Loc. cit.
[11] Kunkel: Handbuch der Toxicologie, vol. i., p. 423.

reaction by means of which its presence even in the most minute traces can easily be detected.[12]

Furfural in dilute solutions has a taste which is not unpleasant and resembles that of benzaldehyde. This latter substance has a taste of bitter almonds and is constantly used for flavouring liqueurs and artificially concocted brandies and other spirits. Benzaldehyde is distinctly poisonous and its use for this purpose is not to be recommended. Furfural has been the subject of a good deal of pharmacological work.[13] It is about 50 times as poisonous as ordinary ethylic alcohol and gives rise in adequate quantities to epileptiform convulsions, general muscular paralysis ending in paralysis of the respiratory muscles, and death. In the body furfural is oxidised to pyromucic acid which substance is physiologically inactive. The symptoms to which furfural gives rise are practically the same in all animals, but with regard to dose pigeons seem most susceptible to its action. In the higher animals when given on an empty stomach it is absorbed almost as rapidly as when injected sub cutem and it gives rise to complete paralysis of voluntary movement. As the animal recovers from this epileptiform convulsions appear. These convulsions are probably due to irritation of the cortical motor-centres and are thus brought into line with those caused by one of the constituents of absinthe. The exact origin of these convulsions is a matter of interest in that, speaking generally, drugs stimulating the cortical motor-centres stimulate also the psychical centres. For instance, cocaine and belladonna exert a marked stimulating action upon the cortical motor-centres, the effect, however, not extending to convulsions but manifesting itself in restlessness. In larger doses both these drugs, especially belladonna, give rise to a mental condition characterised by mania of a very restless kind. Profound restlessness often follows the consumption of spirits and is difficult to explain simply as the result of ethylic alcohol. It is, further, a fact well known to alienists that epileptic mania, one of the most dangerous forms of mania of which we have any cognisance, often alternates in epileptics with true epileptic convulsions. The relation between mania and convulsions is tersely expressed by a leading alienist in adopting the term "ideational convulsion" for the former. Pure ethylic alcohol, so far as we know, causes neither mania nor con-

[12] Lauder Brunton and Tunnicliffe: THE LANCET, Dec. 8th, 1900, p. 1643. It is interesting to note that this colour reaction was formerly taken as indicative of "fusel oil."

[13] Curci: Ricerche Farmacologiche sulla Serie Furfurica, reprint from La Terapia Moderna. Lauder Brunton and Tunnicliffe, loc. cit. Cohn: Archiv für Experimentelle Pathologie und Pharmacologie, xxxi., p. 40. Lepine: Comptes Rendus de la Société de Biologie. Jeffrey and Serveaux: Archives de Médecine Expérimentales, 1896, p. 195. Laborde: Bulletin de l'Académie de Médecine, xx., 1888: N. 40, p. 170; N. 42, p. 526. Daremberg: Bulletin de l'Académie, 1895, iv.; No. 41, p. 332.

vulsions. The class of bodies which we are now considering —viz., aldehydes—do universally cause convulsions, and there is also evidence that at least one aldehyde—viz., furfural—gives rise to great cerebral excitement, animals to whom it had been administered becoming possessed with "a kind of sad fury."[14] The fact that different kinds of alcoholic drinks produce when freely imbibed different mental states—gay, sad, maudlin, &c.—also points to the conclusion that it is probably the by-products contained in spirituous drinks, rather than the ethylic alcohol itself, which give the special timbre to the mentation of the drinker or drunkard.

These considerations are of some ethical interest in that crimes in public-houses, or, at any rate, committed by persons in the initial stages of alcoholic poisoning, are by no means infrequent. These crimes have two peculiarities : they are generally motiveless, at least when judged by the standard of the sane, and they are committed by persons who have taken sufficient drink to affect their minds but not enough to paralyse their muscles. This latter fact shows that the actual amount of alcohol consumed has not been great. The crimes seem to have been committed under the influence of some mental aberration. We know that alcohol paralyses control and therefore it is conceivable that supposing a man had a grudge against his neighbour, although he might normally be able by exercising control to keep his hands off him, yet if he took a glass of pure alcohol and then found himself in the same public-house with the obnoxious acquaintance the alcohol would have so paralysed his control that he would proceed to attack the object of his dislike. The case, however, is quite different when, as sometimes happens, the two combatants were until the liquor was drunk apparently the best of friends and then suddenly under the influence of distorted imagination fell upon one another, often with the most disastrous results. When arraigned before the magistrate the next morning the excuse made by the prisoner for his conduct is that he was under the influence of drink. He was ; but we very much doubt whether he was under the influence of ethylic alcohol.

With regard to the presence in whisky of aldehydes other than furfural and their physiological action very little is known. Ordinary aldehyde was found in a 25 years' old brandy to the extent of 0·0003 per cent.[15] Compound ethers, chiefly ethyl acetate, were present in the same brandy to the amount of 0·042 per cent. Acetic aldehyde (CH_3COH) has physiologically an irritant action upon all the mucous membranes and when absorbed causes, first, irritation of the central nervous system and subsequently complete anæs-

[14] Curci, quoted by Lauder Brunton (evidence before Select Committee, 1891).

[15] Ordonneau : Comptes Rendus, cii., 217, quoted by Allen, Organic Commercial Analysis, vol. i., p. 149.

thesia. Death takes place from asphyxia due to respiratory failure. Another aldehyde present in raw spirit is croton-aldehyde.[16] This substance is also poisonous and when taken in approximately the same quantities as furfural causes great irritation and strong tremors. These tremors are of interest with regard to the work of Sten Stenberg [17] who investigated the difference between the acute alcoholic intoxications produced by raw potato spirit, potato spirit purified by being filtered through charcoal, and pure ethylic alcohol. All the liquids given contained equal quantities of ethylic alcohol, so, therefore, the difference between them was presumably simply one of by-products. The difference in the symptoms produced was not great ; it was *a priori* to be expected that it would not be. Nevertheless, it is evident from the experimental protocols, though apparently unnoticed by the investigator himself, that the occurrence of tremors was more common in the case of the raw potato spirit and the potato spirit purified by means of charcoal than in that of the pure ethylic alcohol. Experiments made recently [18] upon acute alcoholic intoxication by means of ordinary and dealdehyded spirit have shown that the return from the state of intoxication to the normal is different in the two cases, being in the case of the spirit containing aldehydes longer and accompanied by secondary symptoms—e.g., refusal of food, restlessness, and bad temper.

These specific facts, taken into consideration with the general physiologico-chemical properties of the aldehydes, especially their tendency to form compounds with proteids differing essentially from the original substances [19] and the fact that, even if taken in doses apparently incapable of producing symptoms, they are oxidised in the body to acids and thus diminishing the alkalinity of the blood tend to produce the phenomena of acid intoxication, certainly lead us to the conclusion that if they are not necessary for the production of whisky they are much better out of it.

This leads us to a discussion of the manner and the extent of the relationship, if any, between the aldehydes and the bouquet-giving substances in whisky. It must first of all be noted in this connexion that whisky produced from dealdehyded low wines will be freed from both aldehydes and also acetals. It behoves us, therefore, to consider the probable effect upon the ultimate bouquet of whisky of the removal of both these classes of bodies. There can be no doubt concerning the effect of this treatment of the low wines upon the immediate taste of the whisky. Instead of the whisky

[16] Kunkel: loc. cit., vol. i., p. 465.

[17] Archiv für Experimentelle Pathologie und Pharmakologie, vol. x., p. 355 et seq.

[18] Lauder Brunton and Tunnicliffe, loc. cit.

[19] For literature of this subject *vide* Tunnicliffe and Rosenheim on the Influence of Formic Aldehyde upon the Metabolism of Childrens Journal of Hygiene, July, 1901.

appearing as a nauseating and irritant liquid it occurs certainly as an inoffensive drink. Alhehydes as such, speaking generally, are not possessed of an agreeable flavour. The lower aldehydes are, of course, notoriously irritating and so must those, *ex hypothesi*, be which are removed from raw whisky. This can easily be demonstrated by decomposing with dilute mineral acid the hydrazones formed by treating raw whisky with phenyl-hydrazine-sodium-sulphonate and left behind upon subsequent distillation. The original aldehydes are by this method liberated and have a pungent and irritating odour closely resembling that of the original whisky. With regard to the higher aldehydes it is known that in certain instances they occur as a constituent of the ethereal oils of certain fruits. Our knowledge upon this subject, however, is indefinite, although there seems no doubt that two substances known as citral and citronellal are used extensively in the manufacture of artificial perfumes. These substances, however, have never been demonstrated in whisky, raw or matured, and there is no reason to assume that they play any part in its flavour.

It is a known fact that there is now on the market a large assortment of artificially concocted fruit essences. These are largely used in the manufacture of so-called temperance beverages and in cookery, and they impart to the substances to which they are added a flavour almost identical with the fruit, as indicated on the label, to which they correspond. Although the composition of some of these essences is kept a secret the ingredients of the majority of them are known. The compound ethers are their most important constituents and are almost invariably associated with glycerine and occasionally with tartaric, succinic, or benzoic acids. Aldehyde—acetic aldehyde—is also made use of in some of these preparations, but it is difficult to see what purpose it serves, as it is admitted that both it and chloroform, which is also used, can be omitted without serious detriment to the flavour of the essence.[20] A study, then, of the composition of these essences leads us to the conclusion that aldehydes, speaking generally, are not likely to be intimately concerned in the development of bouquet.

With regard to the acetals it is an undoubted fact that these substances are intimately associated with the development of bouquet in wine. As was, however, pointed out earlier in this paper no analogy can *a priori* be assumed between the ageing of wine and the maturation of whisky. That the bouquet of mature whisky owes little, if anything, to acetal is certainly to be assumed from the fact that although it has been recognised as a constituent of mature spirits one of the greatest workers in this country upon this subject frankly asserts that he has never been able to demonstrate its presence in either raw or mature whisky.

[20] Quoted from Allen, loc. cit., p. 215.

Nobody, so far as we know, has ever isolated it from raw whisky. With regard to the acetal corresponding to furfural we have no knowledge nor have we been able to obtain any information. That furfural undergoes but little change during maturation is evident from the fact that the quantitative estimations of it in raw and mature whisky differ but slightly. This difference, furfural apparently diminishing with age can certainly be explained by its evaporation—the assumption that some furfural has been fixed or oxidised is entirely gratuitous. It must further be remembered that the acetals are unstable bodies and in the presence of dilute acids readily decompose into the corresponding alcohol and aldehyde.

Conclusions.

From the above considerations we seem justified in concluding that the aldehydes to which the initial irritating taste and flavour of raw pot-still whisky must be ascribed are only indirectly—viz., by their disappearance—concerned with the ultimate bouquet of old whisky. It further appears that since at least some of the energy of maturation is spent upon the disappearance of these substances it is probable that an initially dealdehyded spirit will become mature in a shorter time than an ordinary one. The last conclusion that we would draw is that since the aldehydes and furfural do not seem necessary for the production of whisky they are from the point of view of the public health better removed from it.

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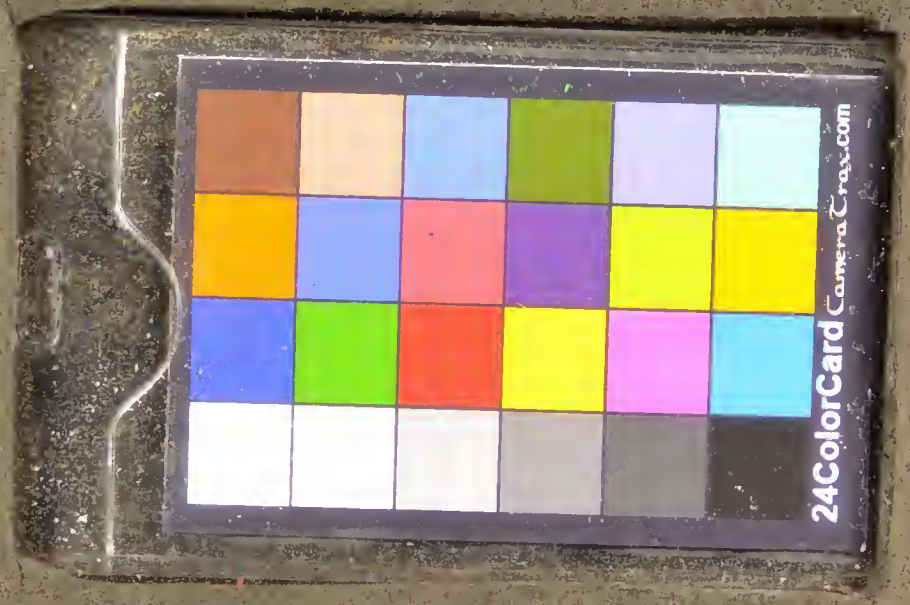
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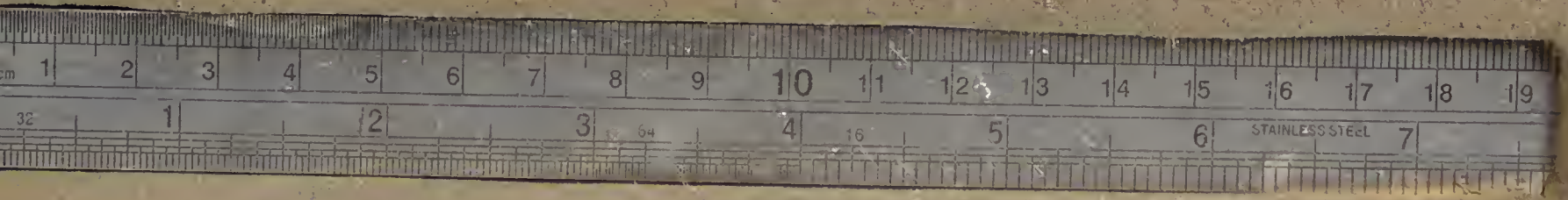
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